
Name of Organization: University of Wisconsin

Type of Organization: College or University

Contact Information: Dr. James Hurley
University of Wisconsin - Water Resources Institute
1975 Willow Dr. - Goodnight Hall
Madison WI 53706

Phone: (608) 262 - 1136 **Extension:**

Fax: (608) 262 - 0591

E-Mail: hurley@wri.wisc.edu

Project Title: Mercury Bioavailability from Lake Superior AOC Sediments

Project Category: Contaminated Sediments

Rank by Organization (if applicable): 0

Total Funding Requested (\$): 186,780 **Project Duration:** 2 Years

Abstract:

James P. Hurley, Lisa B. Cleckner, Kristofer R. Rolfhus and David P. Krabbenhoft
University of Wisconsin-Madison

Abstract

Several fish consumption advisories have been issued for the Great Lakes Basin due to elevated mercury (Hg) concentrations in fish. For Lake Superior, sources and fate of Hg are of particular concern since innovative policies such as "virtual elimination" and "zero discharge" have been adopted and implemented as goals for the ecosystem. In order to understand the biogeochemical cycling of Hg it is essential to determine its reactivity, bioavailability, and transport in sediments, which can be a potential source and sink for Hg in the lake. Physical and chemical characteristics of sediments vary widely and may differentially supply bioavailable Hg to the aquatic food web. This proposed study will compare the forms and fluxes of Hg in sediments from two urban-influenced areas of concern (Duluth-Superior Harbor and Thunder Bay) to those collected from a relatively unimpacted region of the lake, the Apostle Islands. Sediments will be separated into solid and pore water phases and analyzed for total and methyl Hg. Further, simultaneous Hg methylation and demethylation rates will be measured using recently developed stable isotope techniques. Finally, uptake of Hg species from sediments by biota will be assessed using oligochaete bioassays in a controlled laboratory setting. These results will be incorporated into a model currently under development to characterize whole lake Hg cycling. Determination of Hg reactivity in contaminated sediments and subsequent uptake into the trophic structure is critical for developing lakewide management plans for toxic elements in the Lake Superior Basin.

Geographic Areas Affected by the Project

States:

<input type="checkbox"/> Illinois	<input type="checkbox"/> New York
<input type="checkbox"/> Indiana	<input type="checkbox"/> Pennsylvania
<input checked="" type="checkbox"/> Michigan	<input checked="" type="checkbox"/> Wisconsin
<input checked="" type="checkbox"/> Minnesota	<input type="checkbox"/> Ohio

Lakes:

<input checked="" type="checkbox"/> Superior	<input type="checkbox"/> Erie
<input type="checkbox"/> Huron	<input type="checkbox"/> Ontario
<input type="checkbox"/> Michigan	<input type="checkbox"/> All Lakes

Geographic Initiatives:

<input type="checkbox"/> Greater Chicago	<input type="checkbox"/> NE Ohio	<input type="checkbox"/> NW Indiana	<input type="checkbox"/> SE Michigan	<input type="checkbox"/> Lake St. Clair
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Primary Affected Area of Concern: St. Louis River, MN

Other Affected Areas of Concern: Thunder Bay, ONT

For Habitat Projects Only:

Primary Affected Biodiversity Investment Area:

Other Affected Biodiversity Investment Areas:

Problem Statement:

The cycling and transport of mercury (Hg) in freshwater systems has received considerable attention over the past fifteen years due to widespread issuances of fish consumption advisories (40 states, U.S. EPA 1998). While most advisories have been issued for small lakes located in the upper Midwest of the United States, high Hg levels (>0.5 ppm) have also been found in several fish species of Lake Superior. Furthermore, several areas of concern (AOCs) around the Great Lakes have impaired uses due to high Hg levels found in fish and wildlife, including the St. Louis River and Thunder Bay, ON. For remote lakes, atmospheric deposition has been identified as the major source of Hg. However, for Lake Superior and the St. Louis River, other potential sources of Hg include geochemical weathering, watersheds, direct discharges from wastewater treatment plants and industries, and contaminated sediments.

The biogeochemical cycling of Hg in sedimentary environments must be investigated for several reasons. First, sediments act as a sink for Hg in aquatic ecosystems due to particulate scavenging processes and subsequent settling. Second, methylation [i.e., conversion of inorganic to methyl Hg (MeHg)] occurs predominantly at the sediment/water interface, and is mediated by sulfate-reducing bacteria (Compeau and Bartha 1985; Gilmour et al. 1992). Methyl Hg bioaccumulates through the trophic structure of aquatic systems, with nearly 100% of the Hg found in predatory fish present as MeHg (Bloom 1992). Finally, Hg can be released from the sediments into overlying waters through several physical, chemical, and biological processes.

Sediment characteristics can affect Hg solid-aqueous partitioning, as Hg species form strong complexes with both organic matter and inorganic sulfide. Thus, organic-rich or sulfidic sediments tend to bind Hg more strongly than sediments dominated by non-sulfidic inorganic phases. The chemical speciation of aqueous Hg also strongly affects its partitioning characteristics. For example, Hg-polysulfide and Hg-dissolved organic carbon (DOC) complexes can greatly enhance Hg dissolution from inorganic solids (Ravichandran et al. 1998). Mercury species used in industrial processes (and likely present at some AOCs including the St. Louis River and Thunder Bay) may be in forms that are highly immobile and not available for methylation, uptake by biota, or release to the water column (e.g., organomercurials such as phenyl mercuric acetate). Therefore, it is difficult to predict the fate of sedimentary Hg without complementary measurements of uptake and methylation rates.

The study of Hg methylation and demethylation processes is currently undergoing a revolution as new ICP-MS analytical techniques are being developed (Hintelmann and Evans 1997). In the past, methylation rates were determined by injecting a radioactive inorganic Hg isotope (²⁰³Hg) into intact cores, and then extracting and analyzing newly formed ²⁰³MeHg following incubation. This measurement provided a "net methylation" rate, as microbial demethylation of ²⁰³MeHg may have simultaneously occurred during the incubation. However, with the use of an ICP-MS and multiple stable isotopes of Hg, simultaneous methylation and demethylation rates may be measured by injecting one isotope of inorganic Hg

[199Hg(II)] and another of organic Hg [201MeHg], and then measuring the formation of the reaction products, 199MeHg, 201Hg(II), and 201Hgo.

Another key step in understanding the fate of Hg in contaminated sediments is determining whether the Hg is available for uptake by benthic organisms found in Lake Superior such as *Diporeia hoyi* and *Mysis relicta*. Benthos comprise a significant fraction of diets for several forage fish species including rainbow smelt and lake herring, and thus act as a transfer point for sedimentary Hg into the aquatic food web (Harvey and Kitchell, in press). Further, organisms living in and near the sediments can facilitate the release of Hg to overlying waters by bioturbation. Little is known about this vector of Hg transfer, but our prior work on Hg cycling in the Florida Everglades indicated that zoobenthos and other invertebrates are intimately associated with both methylation in sediments and fish Hg concentrations on a spatial basis within the ecosystem (Hurley et al. 1998; Gilmour et al. 1998; Cleckner et al. 1998, Krabbenhoft unpublished data).

Proposed Work Outcome:

Widespread emissions and use of Hg in the urban and industrialized regions of the St. Louis River and Thunder Bay may contribute to enhanced Hg entry into aquatic and terrestrial food webs of Lake Superior. Further, near shore sediments (especially those in harbors) represent potentially important sites for Hg methylation due to warmer temperatures and conditions that are more favorable for bacterial activity (e.g., elevated nutrient levels). We propose to determine the importance of contaminated sediments as a potential source of bioaccumulating Hg in Lake Superior fish by measuring Hg concentrations, fluxes, methylation rates, and bioavailability from AOCs. In addition, we will examine similar Hg and sedimentary processes at a relatively unimpacted and shallow site in the Apostle Islands, WI. Such comparisons will enable modelers and resource managers to assess the relative impact of contaminated sediments on fish Hg concentrations.

The goal of our proposed work is to examine the concentrations, fluxes, and subsequent bioavailability of total Hg (HgT) and MeHg from sediments in contrasting near shore areas of Lake Superior. We will couple field measurements of Hg species and ancillaries in aqueous and solid phases of sediment cores with controlled laboratory studies designed to assess in vitro methylation rates and biouptake of Hg species by benthic organisms.

The specific objectives are:

1. Determine the relative bioavailability of sedimentary MeHg and inorganic Hg in contrasting near shore zones, as measured by uptake to benthic invertebrates and the use of chemical resin binding assays.
2. Determine methylation/demethylation rates in intact sediment cores using newly- developed stable isotopic techniques.
3. Estimate fluxes of HgT and MeHg from sediments of contaminated and relatively unimpacted near shore regions.
4. Provide essential information on near shore sediment-water interaction for modeling efforts currently underway in the Lake Superior system.

Approach:

Our experimental design focuses on determining the relationships between sedimentary Hg species content, flux, and bioavailability in near shore sediments that contrast with respect to anthropogenic impact. Research activities will focus on the collection of sediment cores from depositional zones in three locations of Lake Superior: Duluth-Superior Harbor, Thunder Bay (both are contaminated AOCs), and the Apostle Islands, WI.

Physical/Chemical Characterization of Cores and Overlying Water: We plan on collecting 10 replicate sediment cores from a depositional zone within each site for solid phase analysis. The surficial 10 cm from each core will be sectioned into five 2-cm samples, which will be analyzed for MeHg, HgT, total organic carbon (TOC), Fe and Mn, total and thiol sulfur (S), bulk density, temperature, and sediment porosity. Pore waters will be collected from an additional 10 cores using a squeeze-coring technique that has been used successfully on many lakes in Wisconsin (Hurley et al. 1994), and analyzed for Hg species, DOC, Fe/Mn, and total sulfide determinations. Surface and bottom waters will be collected from each location, which will be analyzed for filtered/unfiltered HgT and MeHg, S speciation, and DOC content. Additionally, the chemical reactivity of pore water Hg will be determined using Chelex and XAD resin binding assays, which determine the presence of labile and organically-complexed Hg species, respectively (Mazidji et al. 1992; Ferri and Sangiorgio 1996; Aiken et al. 1992). All sample collection, processing, and storage procedures will follow strict "clean techniques" that have been developed for analysis of trace metals at ambient environmental concentrations (Hurley et al. 1996).

Methylation/Demethylation Rate Determination: An additional 10 replicate sediment core samples will be collected at each location in order to measure the simultaneous, *in vitro* rates of methylation and demethylation. Surficial sediments will be spiked with near-ambient levels (ng L⁻¹) of 199Hg(II) and 201MeHg, incubated at ambient environmental temperature and light intensity for 12 hours, and analyzed by ICP-MS for the respective reaction products, 199MeHg, 201Hgo, and 201Hg(II). We have access to a dedicated Hg-only quadrupole ICP-MS at the U.S. Geological Survey (Middleton, WI) that will allow for inorganic and organic (MeHg) stable isotope determinations in solid and aqueous phases.

Bioavailability: MeHg and Hg(II) Uptake by Benthic Invertebrates: Ten additional cores will be collected from each site in order to provide surficial sediment (top 10 cm) and overlying water for standard laboratory bioaccumulation experiments (Ingersoll et al. 1996). Adult oligochaetes (*Lumbriculus variegatus*) will be incubated with sediment from each of the 10 intact cores and overlying site water in an environmental chamber at ambient temperature and light for 28 days. Following incubation, organisms will be separated from the sediments, placed into a beaker with site water to allow gut clearance, and analyzed for MeHg and HgT. In order to determine the pre-exposure baseline tissue concentration, cultured test organisms will be analyzed for Hg species. Organisms will be cultured and maintained at the Wisconsin State Laboratory of Hygiene Biomonitoring Group. Biouptake will be compared to the sediment Hg concentration results and pore water chemical resin lability assays in order to establish patterns of relative "bioavailability" between the three impacted/unimpacted sites.

Hg Species Sediment-Water Fluxes: The transport of Hg species across the sediment-water interface will be estimated using two techniques: 1) incubation of sediment grab samples with overlying ambient water, and 2) a Fickian diffusion model based upon the measured pore water-bottom water Hg concentration gradient. The waters overlying incubated sediments will be periodically sub-sampled for 0.45 µm filtered HgT and MeHg analysis, and replaced with an equivalent volume of new water. The overlying water will be constantly agitated at perceived ambient mixing rates in order to determine the maximal flux from the sediments.

Modeling: Results from our study will be included in the Tetra Tech Inc. Mercury Cycling Model (R-MCM) that is being developed specifically for Lake Superior. The Electric Power Research Institute has funded Tetra Tech for a period of three years (1999-2001) to develop a derivative of the existing R-MCM for Lake Superior. Our study will address several gaps that exist in our current understanding of sedimentary Hg dynamics, including rates of Hg release from sediments and Hg cycling in the benthic food web. This model will have widespread applicability for research, regulatory, and long-term planning interests in the Lake Superior Basin. We have worked closely with Tetra Tech Inc. in developing models from our previous work on northern Wisconsin lakes and in the Florida Everglades. Sediment-water flux estimates and phase partitioning have been critical components of each of those models.

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Project Milestones:**Dates:**

Project Start	07/2000
Method development, prelim. field work	07/2000
Fall sediment coring effort	09/2000
Laboratory bioassay work, Hg analyses	09/2000
Spring and summer coring efforts	05/2001
Laboratory bioassay and Hg analyses	05/2001
Project Report - first draft	04/2002
Project End	06/2002

☐ Project Addresses Environmental Justice

If So, Description of How:

☒ Project Addresses Education/Outreach

If So, Description of How:

We will develop a web site at the University of Wisconsin that will highlight the research from this project. The recent merger of the University of Wisconsin Water Resources Institute (WRI) and the UW Sea Grant Institute (SGI) provides a strong information technology program, including Earthwatch Radio. The UW Sea Grant Program has won several awards for its outreach-based Web site, and we plan to take full advantage of these capabilities by developing a series of pages dealing with Hg fate and transport in the Lake Superior Basin. An interactive Web-based Internet site devoted to Lake Superior Hg cycling will be developed for the general public.

The WRI-SGI unit has a strong communications department that will allow for dissemination of our results to the general public. Our association with the Wisconsin DNR also provides strong outreach capabilities. For instance, WI DNR coordinated a press release for our initial funding of the USEPA STAR mercury project. Over one thousand outlets in the U.S. and Canada received the release, resulting in numerous newspaper articles and radio interviews. We expect to continue to use this form of information dissemination for the proposed research.

We will also present our results at local (Wisconsin Chapter American Water Resources Association) and national meetings (International Association of Great Lakes Research; American Chemical Society, American Society of Limnology and Oceanography, American Geophysical Union). Our group has given several presentations to federal, state and local groups on our ongoing research on Lake Superior and Isle Royale National Park.

Project Budget:

	Federal Share Requested (\$)	Applicant's Share (\$)
Personnel:	61,670	11,045
Fringe:	12,052	3,590
Travel:	6,000	0
Equipment:	0	0
Supplies:	20,000	6,000
Contracts:	30,000	0
Construction:	0	0
Other:	0	0
Total Direct Costs:	129,722	20,635
Indirect Costs:	57,058	0
Total:	186,780	20,635
Projected Income:	0	0

Funding by Other Organizations (Names, Amounts, Description of Commitments):

Our current project "Watershed Influences on Transport, Fate and Bioavailability of Mercury in Lake Superior", (Project Period: October 1, 1999 - September 30, 2002; Project Cost: \$829,383; Principal Investigator: J.P. Hurley; Co-Investigators: R. Back, D. Armstrong and M. Shafer; USEPA-STAR) is currently in its first year of funding. The project focuses on watershed and riverine influences on Hg cycling and bioavailability in Lake Superior and its tributaries. Significant effort on the EPA-STAR project addresses near shore mixing zones from rivers draining contrasting land use/land cover types. Most of the rivers chosen for study are in relatively unimpacted watersheds. In contrast, the work in this proposal focuses intensively on contaminated sediments and benthic processes influencing bioavailability of Hg. Data collected from this project will be very complementary to our EPA-STAR research, and results from all phases of our research will be important components of a separately funded (by the Electric Power Research institute) modeling effort by Tetra Tech, Inc. Development of the Lake Superior Mercury Cycling Model will enable predictive capabilities for management concerns in the basin.

Costs for web page development and information technology will be provided by the University of Wisconsin (see Outreach/Education section above). Non-federal match for salary (J. Hurley, 1 month) and supplies will be provided. One month of Dr. Hurley's salary and \$3000 per year for supplies (non-federal funds will be matched) against this project.

Description of Collaboration/Community Based Support:

We will continue to interact and inform community and regionally based groups within the basin, such as the Lake Superior Binational Forum, on our results and progress. Fish consumption advisories for mercury continue to be posted for Lake Superior, and it is important to understand the reasons for bioaccumulation of Hg as a Level 1 contaminant of concern. Understanding the bioavailability of Hg in contaminated zones of Lake Superior is a key to developing management strategies including "zero discharge" and "virtual elimination" of toxins in the basin. The predictive capabilities of the associated Tetra Tech "Lake Superior Mercury Cycling Model" is important for determining the effects of changing atmospheric and point-source loading to the lake. Similar to our EPA STAR proposal, the WI DNR representative to the Lake Superior Binational Program supports our efforts.